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(54) Nonaqueous cell and a method for treating an active metal anode of a nonaqueous cell.

(57) A nonaqueous cell employing a liquid active cathode, such as thionyl chloride, and an anode, such as lithium, coated with a boron-containing surface film that will substantially prevent excessive anode passivation during storage or discharge of the cell.

The term "nonaqueous electrolyte" as used herein refers to an electrolyte which is composed of a solute, such as, for example, a metal salt or a complex salt of Group IA, Group IIA, Group IIIA or Group VA elements of the Periodic Table, dissolved in an appropriate nonaqueous solvent. The term "Periodic Table" as used herein refers to the Periodic Table of Elements as set forth on the inside front cover of the Handbook of Chemistry and Physics, 63rd Edition, CRC Press Inc., Boca Raton, Florida, 1982-1983.

A multitude of solutes is known and many have been suggested for use but the selection of a suitable solvent has been particularly troublesome. The ideal battery electrolyte would comprise a solvent-solute pair which has a long liquid range, high ionic conductivity and stability. A long range, i.e., high boiling point and low freezing point, is essential if the battery is to operate at other than normal ambient temperatures. High ionic conductivity is necessary if the battery is to have high rate capability. Stability is necessary with the electrode materials, the materials of cell construction, and the products of the cell reaction to provide long shelf life when used in a primary or secondary battery system.

It has recently been disclosed in the literature that certain materials are capable of acting both as an electrolyte carrier, i.e., as solvent for the electrolyte salt, and as the active cathode for a nonaqueous electrochemical cell. US-A 3,475,226, US- 3,567,515, and US-A 3,578,500 each disclose that liquid sulfur dioxide or solutions of sulfur dioxide and a cosolvent will

voltage delays at the beginning of discharge along with high cell impedance.

5 US-A 3,993,501 discloses one approach for minimizing or preventing undesirable voltage delays at the beginning of discharge of nonaqueous cells employing an oxyhalide-containing cathode-electrolyte by providing a vinyl polymer film coating on the surface of the anode that contacts the cathode-electrolyte.

10 US-A 4,218,523 discloses a nonaqueous cell comprising an active metal anode, such as lithium, a liquid cathode-electrolyte comprising a solute dissolved in a solvent which is an oxyhalide of an element of Group V or Group VI of
15 the Periodic Table and wherein elemental sulfur or a sulfur compound is incorporated into the cathode-electrolyte so as to substantially eliminate initial voltage delay of the cell during discharge.

20 US-A 4,277,545 discloses a nonaqueous cell utilizing an active metal anode, such as lithium, a cathode collector and an ionically conductive cathode-electrolyte comprising a solute dissolved in a liquid cathode, such as an oxyhalide, and wherein a vinyl polymer is dissolved
25 in the cathode-electrolyte so as to substantially eliminate initial voltage delay of the cell during discharge.

30 US-A 4,020,240 discloses an electrochemical cell employing an electrolyte salt containing a clovoborate anion structure which functions to retard anode passivation during long time storage even at elevated temperatures.

US-A 4,071,664 discloses an electrochemical cell comprising an active metal

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eliminate excessive passivation of the anode when it is contacted with a nonaqueous electrolyte, such as an oxyhalide electrolyte.

The foregoing and additional objects will
5 become more fully apparent from the following description:

Disclosure of the Invention:

The invention relates to a nonaqueous electrochemical cell comprising an active metal
10 anode, a cathode and an ionically conductive electrolyte solution containing a solute dissolved in a nonaqueous solvent and wherein said solute consists of a salt of a first component of a halide of an element selected from the group consisting of
15 Al, Sb, Zr, and P, and a second component of a halide, sulfide, sulfite, oxide or carbonate of calcium or an alkali metal selected from the group consisting of Li, Na, and K; and wherein said active metal anode has a surface layer of a boron-
20 containing material thereon.

The invention also relates to a method for treating an active metal anode and assembling the precoated anode along with a cathode and a nonaqueous electrolyte to produce a cell, which
25 comprises:

(a) preparing a boron-containing material, such as $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, in a liquid medium, such as SOCl_2 ;

(b) placing an active metal anode, such as
30 lithium, in the boron-containing liquid medium for a time period sufficient to form a boron-containing film on at least a portion of the surface of the anode; and

when employed in a nonaqueous cell, preferably a cell employing a liquid cathode such as thionyl chloride. The boron-containing salt could be added in any amount in solution as long as it is

5 sufficient to form a layer of the boron-containing material on the anode. An anode, such as lithium, could be placed in the solution containing the closoborate anion for a period of time sufficient to

10 adequately coat the surface of the anode with the boron-containing material. Exposing the anode in the solution for an excessively long period may not provide any additional benefit with regard to preventing excessive passivation of the anode when exposed in a nonaqueous solution. However, it

15 should be realized that the period the anode is exposed in the boron-containing solution will depend on the type of solution employed, the concentration of the boron-containing material in the solution, the composition and condition of the anode surface

20 and the temperature of the solution.

Boron-containing materials which are known in the chemical literature and as disclosed in US-A 4,071,664, and which would be useful in this invention are $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, $\text{Li}_2\text{B}_{10}\text{Br}_{10}$,

25 $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$, $\text{Li}_2\text{B}_{12}\text{I}_{12}$, $\text{Li}_2\text{B}_6\text{Br}_6$, $\text{Li}_2\text{B}_{12}\text{Br}_8\text{F}_4$, $\text{Li}_2\text{B}_9\text{Cl}_8\text{H}$, $\text{Li}_2\text{B}_9\text{Cl}_9$, $\text{Li}_2\text{B}_9\text{Br}_6\text{H}_3$, $\text{Li}_2\text{B}_{11}\text{Br}_9\text{H}_2$, $\text{Li}_2\text{B}_{12}\text{H}_8\text{F}_4$, $\text{Li}_2\text{B}_{12}\text{H}_7\text{F}_5$, $\text{Li}_2\text{B}_{12}\text{H}_6\text{F}_6$ and $\text{Li}_2\text{B}_{12}\text{F}_{11}\text{OH}$. The preferred material would be $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, $\text{Li}_2\text{B}_9\text{Cl}_9$ and

30 $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$. Other types of boron-containing material which may be useful in this invention are boron oxides, boron halides, boron sulfides, boron phosphates, boron sulfates, boron sulfites and boron hydrides.

The use of a single component of the cell as both an electrolyte solvent and active cathode (depolarizer) is a relatively recent development since previously it was generally considered that the two functions were necessarily independent and could not be served by the same material. For an electrolyte solvent to function in a cell, it is necessary that it contact both the anode and the cathode (depolarizer) so as to form a continuous ionic path therebetween. Thus it has generally been assumed that the active cathode material must never directly contact the anode and, therefore, it appeared that the two functions were mutually exclusive. However, it has recently been discovered that certain active cathode materials, such as the liquid oxyhalides, do not appreciably react chemically with an active anode metal at the interface between the metal and the cathode material, thereby allowing the cathode material to contact the anode directly and act as the electrolyte carrier. While the theory behind the cause of the inhibition of direct chemical reaction is not fully understood at the present time and the applicant does not desire to be limited to any theory of invention, it appears that direct chemical reaction is inhibited either by an inherently high activation energy of reaction or the formation of a thin, protective film on the anode surface. Any protective film on the anode surface must not be formed to such an excess that a large increase in anode polarization results.

Although the active reducible liquid cathodes, such as the oxyhalides, inhibit the direct reaction of active metal anode surfaces sufficiently

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In accordance with the present invention, it has been found that excessive anode passivation can be substantially prevented by treating the anode with a boron-containing material so as to form on the surface of the anode a layer or film of a boron-containing material. Although not wanting to be bound by theory, it is believed that when treating lithium anodes, a lithium boride layer is formed on the surface of the anode which will retard excessive passivation of the anode when placed in a liquid oxyhalide solution such as a thionyl chloride solution. Accordingly, boron oxides, halides, sulfides etc, would probably boride the surface of a lithium anode easier than the closoborates since removal of boron from most of these materials through reaction with the lithium metal would occur more readily than from the rather stable closoborates. It is also believed that the boride layer formed on the anode is insoluble in an oxyhalide solution.

The active liquid reducible cathode material (depolarizer) for use in this invention can either be mixed with a conductive solute which is a nonreactive material but is added to improve conductivity of the liquid active reducible cathode materials, or it can be mixed with both a reactive or nonreactive conductive solute and a reactive or nonreactive cosolvent material. A reactive cosolvent material is one that is electrochemically active and, therefore, functions as an active

and may be present in any physical form, such as a metallic film, screen or a pressed powder. Preferably, however, a pressed powder collector should be made at least partially of carbonaceous or other high surface area conductive material.

5 The solute may be a simple or double salt which will produce an ionically conductive solution when dissolved in the solvent. Preferred solutes are complexes of inorganic or organic Lewis acids and inorganic ionizable salts. The main requirements for utility are that the salt, whether simple or complex, be compatible with the solvent being employed and that it yield a solution which is ionically conductive. According to the Lewis or
10 electronic concept of acids and bases, many substances which do not contain active hydrogen can act as acids or acceptors of electron doublets. The basic concept is set forth in the chemical literature (Journal of the Franklin Institute, Vol. 226 - July/December, 1938, pages 293-313 by G. N. Lewis).

A suggested reaction mechanism for the manner in which these complexes function in a solvent is described in detail in US-A
25 3,542,602 wherein it is suggested that the complex or double salt formed between the Lewis acid and the ionizable salt yields an entity which is more stable than either of the components alone.

Typical Lewis acids suitable for use in the present invention include aluminum fluoride,
30 aluminum bromide, aluminum chloride, antimony pentachloride, zirconium tetrachloride, phosphorus pentachloride, boron fluoride, boron chloride and boron bromide.

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Example

Two lithium anodes measuring 33,0 x 10,7 mm (1.3 inches by 0.42 inch) were placed in a 0.25M $\text{Li}_2\text{B}_{10}\text{Cl}_{10}\text{-SOCl}_2$ solution for 14 days at 25°C. Each of the treated anodes was then assembled in a 1,2 mm (0.475 inch) diameter container along with a nonwoven glass fiber separator and a cathode-electrolyte comprising 1.5M $\text{LiAlCl}_4\text{-SOCl}_2$ solution. A similar cell was produced except the anode was untreated. The three cells so formed were stored for 45 days at 25°C and then each cell was discharged across a 75 ohm load. The voltage data obtained versus time are shown in the table .

Table				
15	Voltage (volts)			Time (sec)
	Untreated Anode	Treated Anodes		
		Cell A	Cell B	
20	3.67	3.67	3.67	0
	1.05	2.83	2.83	1
	1.07	2.91	2.88	2
	1.11	2.95	2.91	5
	1.20	2.93	2.92	10
	1.28	2.93	2.93	15
	1.35	2.94	2.94	20
	1.42	2.95	2.95	30

- 1 4. The method of claim 3, characterized in that in
step (a) the boron-containing material is selected
from the group consisting of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, $\text{Li}_2\text{B}_9\text{Cl}_9$
and $\text{Li}_2\text{B}_{12}\text{Cl}_{12}$; in step (b) the anode is selected
5 from the group consisting of lithium, sodium, cal-
cium, potassium, and aluminum; and in step (c) the
cathode is a liquid cathode selected from the group
consisting of thionyl chloride, sulfuryl chloride,
phosphorous oxychloride, thionyl bromide, chromyl
10 chloride, vanadyl tribromide, selenium oxychloride,
selenium tetrafluoride, selenium monobromide, thio-
phosphoryl chloride, thiophosphoryl bromide, vana-
dium pentafluoride, lead tetrachloride, titanium
tetrachloride, disulfur decafluoride, tin bromide
15 trichloride, tin dibromide dichloride, tin tri-
bromide chloride and liquid SO_2 .
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